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The Dielectric Relaxation of γ-Alumina[1]

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The dielectric constant of high-purity γ-alumina, synthesized in this laboratory and having the specific surface area of 220 m^2/g, was measured in the frequency range from 30 Hz to 3 MHz and 9.72 GHz and at temperatures ranging from 120 to −196 °C. About 180 °C was found reasonable as the desorption temperature of the water adsorbed on γ-alumina. Three dielectric relaxations, I, II, and III, were found, and some inferences were given as to their mechanism in relation to loosely-adsorbed water, a surface hydroxyl group which can be easily dehydrated, and some other kind of hydroxyl group with a weak interaction with its neighbors, respectively.

The study of the dielectric relaxation of metallic oxides of high specific-surface areas, such as alumina and silica, gives us useful information on their surface states. The dielectric studies of γ-alumina reported by several authors[2-5] have been mainly related to the electric polarization of the adsorbed water and their interaction with the surface of γ-alumina. It seems of primary necessity to know the properties of the surface of the adsorbent itself in order to study the dielectric behavior of the adsorbed molecules and their interaction with the adsorbent surface. In order to secure a fresh and bare surface of the adsorbent, it is necessary to find experimentally the desorption temperature of adsorbed water, which has been chosen empirically in most cases.

Some of the previous authors[2-4] seemed to find the dielectric relaxations of γ-alumina with adsorbed water, and attributed the relaxations to the adsorbed water. In order to discuss the mechanism of the dielectric relaxation, it seems necessary, however, to study it over wider range of frequency and temperature.

The present investigation was carried out along these lines on well-defined γ-alumina of a high purity and a high specific-surface area.

Experimental

Material. γ-Alumina with very low alkali and alkali-earth ion concentrations was prepared according to the ordinary procedures.[6-8] Colloidal aluminum hydroxide, precipitated from a 16 wt% solution of anhydrous aluminum trichloride by adding enough 4 M ammonium hydroxide, was washed carefully to remove any ammonium chloride. This material was then transformed to Bayerlite crystals by aging it for about 15 days at pH 9 and 15 °C. The material thus obtained was calcined at about 600 °C and was then transformed to γ-alumina, which was identified by means of its X-ray diffraction pattern. The particle size of this material was observed to be about 2×10^2 Å by the electron microscope, and the specific-surface area was found to be 220 m^2/g by the BET N_2 method. 3 ppm of Na^+, 130 ppm of Fe^{3+}, and no other cations were found in the γ-alumina by the spectroscopic analysis of the metal cations, such as Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, and Fe^{3+}.

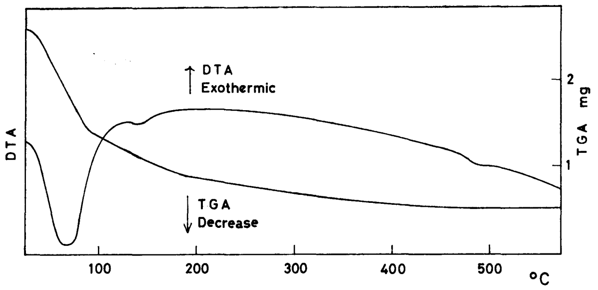

Fig. 1. The DTA and TGA curves of γ-alumina in the atmospheric air with the heating rate of 10 °/min.

The DTA and TGA measurements were carried out using a thermal-analysis instrument of the Rigaku Denki Co., Type CSL-8001; the measuring conditions, such as the heating rate, the atmosphere, the thermal history, and the hydration-dehydration cycle of the sample, were carefully varied. The results with a heating rate of 10 °/min in atmospheric air are shown in Fig. 1. A broad endothermic DTA peak appeared at about 60 °C, accompanied by a large weight-decrease from room temperature to about 90 °C, while a smaller weight-decrease of about 2% followed to the neighborhood of 190 °C. From about 190 °C to about 500 °C, the weight-decrease was much smaller, and the decrease became even smaller above 500 °C. From these TGA and DTA curves, it is difficult to find the exact temperature of the desorption of adsorbed water. However, it is reasonable to set the desorption temperature as 180 °C, as concluded from the $\tan \delta$ versus temperature relations shown in Figs. 8 and 11. The γ-alumina used for the dielectric measurement contained various amounts of adsorbed water ranging from 0 to 12%, or was heated at 250, 280, and 300 °C for 2 hr in a vacuum before measurement. Figure 2 shows the water-adsorption isotherm of this material at 15 °C. The deuterium was exchanged with the γ-alumina according to a method described elsewhere[9] in order to see the isotope effect of the dielectric relaxation.

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[1] Presented at the spring annual meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] Von G. Ebert and G. Langhamer, *Kolloid Z.* **174**, 5 (1961); Von G. Ebert, *ibid.*, **174**, 158 (1961).

[3] K. Dransfeld, H. L. Frisch, and E. A. Wood, *J. Chem. Phys.*, **36**, 1574 (1962).

[4] M. G. Baldwin and J. C. Morrow, *J. Chem. Phys.*, **36**, 1591 (1962).

[5] R. Kiriyama, H. Kiriyama, K. Hiwada, and N. Kawai, the 22nd Colloid Symposium of the Chemical Society of Japan at Sendai, 1969.

[6] K. Sakamoto, *Yogyo Kyokai-shi*, **67**, C114 (1959).

[7] K. Funaki and Y. Shimizu, *Denki-Kagaku*, **28**, 302 (1960); K. Funaki and Y. Shimizu, *ibid.*, **28**, 358 (1960).

[8] G. Yamaguchi, *Kagaku to Kogyo*, **17**, 1326 (1964).

[9] S. Kondo and M. Muroya, This Bulletin, **42**, 2724 (1969).

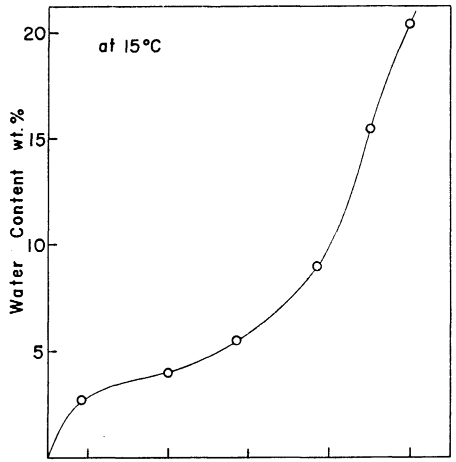

Fig. 2. The water adsorption isotherm of γ-alumina at 15 °C.

Dielectric Measurements. The complex dielectric constant and tan δ were measured using the transformer-bridge method, in the frequencies from 30 Hz to 3 MHz and using the transmission-line method, at 9.72 GHz. The design and the materials of the cell electrodes, the heating and cooling devices, and the measuring procedures employed in this experiment were the same as those in the previous papers.[10,11]

Results and Discussion

Three dielectric anomalies were found to exist in different frequency and temperature ranges on γ-alumina with and without adsorbed water; some of these results at 30 and 300 kHz are shown in Fig. 3. In the figure, three anomalies, I, II and III, are clearly seen at different temperatures. Anomaly II agrees approximately with that found by Ebert[2] and by Dransfeld.[4] These anomalies were dependent on the frequency, the temperature, and the water content.

Anomaly I. Figures 4 and 5 show the frequency effect of ε' and tan δ at 55 °C, and the Cole-Cole arc plot of Anomaly I at 3% water, respectively. These figures show that this anomaly is a dielectric relaxation (Relaxation I), although it seems difficult to tell whether Relaxation I is of the Debye-type or the Wagner-type. It seems clear that Relaxation I has some relation with the proton in such forms as the ion, the hydroxyl group on the surface, and the adsorbed water, since the relaxation times shift markedly upon the deuterium exchange, as is shown in Fig. 6. The relation between

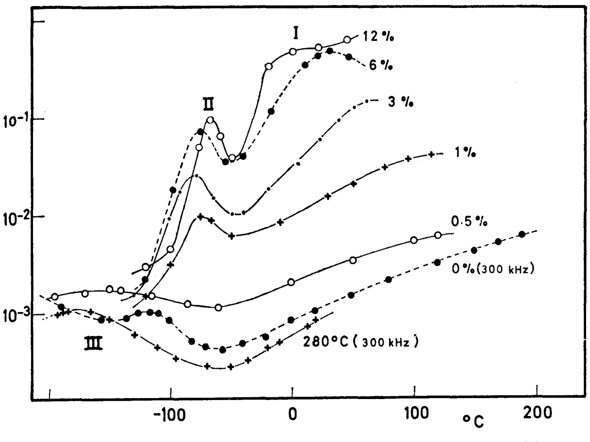

Fig. 3. The relations between temperature and tan δ at 30 kHz and 300 kHz of γ-alumina with various amount of adsorbed water and with heat-treatment, respectively.

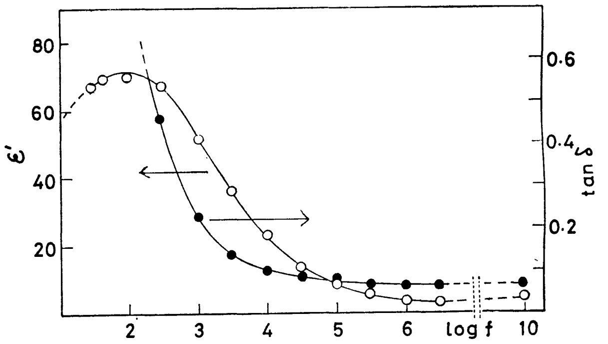

Fig. 4. The ε' and tan δ *versus* frequency curves of γ-alumina in the range of the dielectric relaxation I containing 3% water at 55 °C.

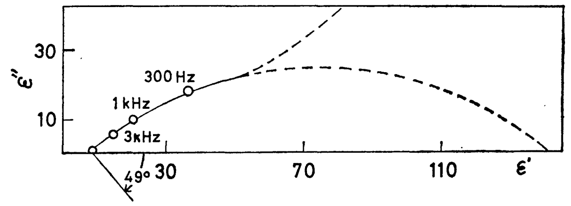

Fig. 5. The Cole-Cole arc of the Relaxation I of γ-alumina containing 3% water at 55 °C.

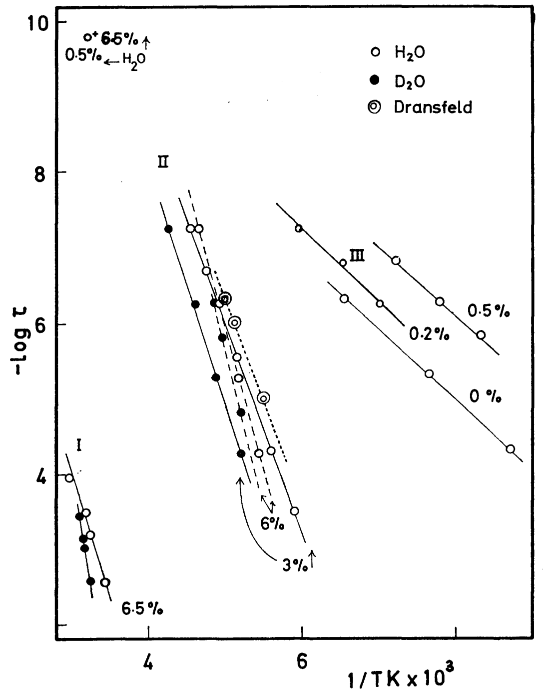

Fig. 6. The relations between logarithum of relaxation times, log τ, of the Relaxations I, II, and III and the reciprocal temperatures on γ-alumina with or without various amount of light and heavy water.

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[10] S. Kondo and M. Muroya, This Bulletin, **42**, 1165 (1969).

[11] S. Kondo and M. Muroya, *Rept. Osaka Electro-Communication Univ.*, **2**, 18 (1966).

Table 1. The activation energy, E, and the coefficient, τ_0, of the Arrhenius equation of the relaxations I, II, and III of γ-alumina

Water content (%)	H_2O E (kcal/mol)	H_2O τ_0 (sec)	D_2O E (kcal/mol)	D_2O τ_0 (sec)
Relaxation I				
12	11.2 ± 0.5	2×10^{-14}		
6	11.6 ± 0.5	3×10^{-13}	12.2 ± 0.5	1×10^{-14}
3	12.1 ± 0.7	1×10^{-12}		
2	12.4 ± 0.7	1×10^{-12}		
1	11.9 ± 0.7	2×10^{-12}		
Relaxation II				
12	20.6 ± 0.5	4×10^{-27}		
6	17.5 ± 0.5	9×10^{-24}	18.8 ± 0.5	2×10^{-26}
3	13.0 ± 0.5	1×10^{-21}	14.4 ± 0.5	2×10^{-21}
2	14.4 ± 0.5	3×10^{-21}		
1	13.2 ± 0.5	3×10^{-18}		
Relaxation III				
0.5	4.1 ± 1.0	2×10^{-13}		
0.2	4.6 ± 1.0	2×10^{-13}		
0	4.7 ± 1.0	2×10^{-13}		

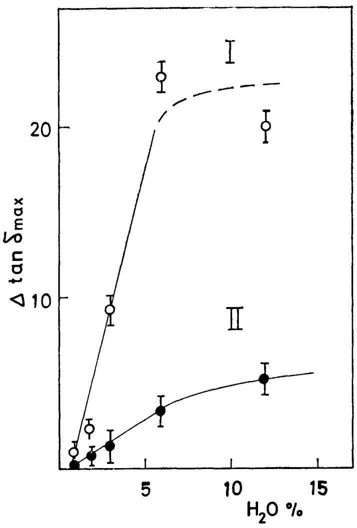

Fig. 8. The relations between the water content and Δ tan δ_{max} which was estimated as the difference of tan δ maxima of the Relaxations I (open circle) and II (full circle) and their baselines.

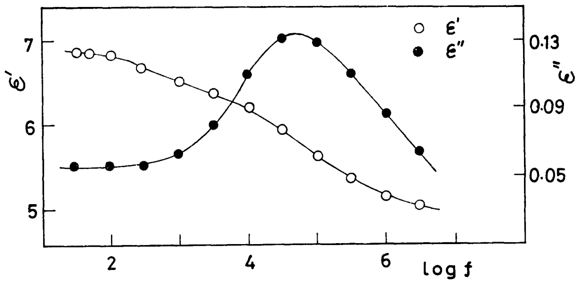

Fig. 9. The relations of ε' and ε'' to the frequency of the Relaxation II of γ-alumina having 3% adsorbed water at −79 °C.

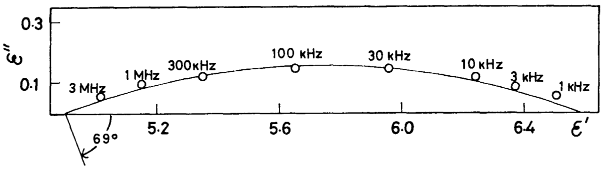

Fig. 10. The Cole-Cole arc of the Relaxation II of γ-alumina containing 3% adsorbed water at −79 °C.

the relaxation times and the reciprocal temperatures, obtained from the Cole-Cole arc plot, is linear, as is shown in Fig. 6. The activation energy, E, and the coefficient, τ_0, in the Arrhenius expression are shown in Table 1. The values of E do not change with the water content, but those of τ_0 do change appreciably. The magnitude of Relaxation I (Δ tan δ_{max}) was estimated from Fig. 7, by subtracting the value of the tan δ maximum from its base line; it is plotted against the water content in Fig. 8. The figure shows that Relaxation I disappears in the neighborhood of 0% water and increases proportionally to the water content up to about the second layer of the adsorbed water (about 6%).

Anomaly II. The relation between the complex dielectric constant and logarithm of frequency, and the Cole-Cole arc plot of Anomaly II at −79 °C, shown in Fig. 3, are given in Figs. 9 and 10 respectively. These curves suggest that this anomaly is a dielectric relaxation of the Maxwell-Wagner type (Relaxation II). The findings by Dransfeld[3] agree approximately with ours. Since Relaxation II showed a marked frequency shift upon the deuterium exchange, as is shown in Fig. 6, this relaxation seems to be related to either some form of adsorbed water or to some kind of hydroxyl group on the γ-alumina surface. The magnitude of Relaxation II (Δ tan δ_{max}) is plotted in Fig. 8 with the same procedure as has been described in the case of Relaxation I. In this figure, Relaxation II behaves similarly to Relaxation I, and both of these relaxations disappear somewhere near 0% water. However, the point of disappearance is not yet known more exactly. The sample heat-treated in the range from 65 to 180 °C, after the saturation of the sample with water at room temperature, contains adsorbed water ranging from 2 to 0% respectively, when we take 180 °C as the desorption temperature. Therefore, it

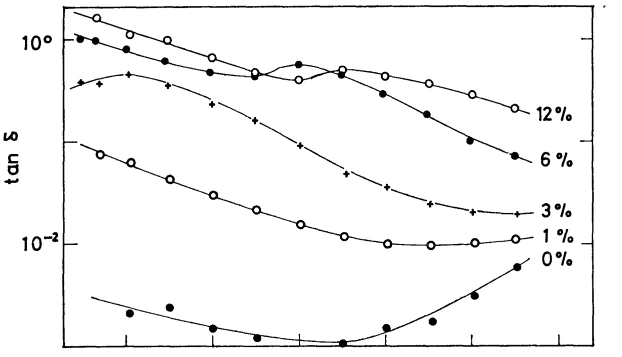

Fig. 7. The curves of frequency versus log tan δ of γ-alumina with various amount of water at 23 °C in the range of Relaxation I.

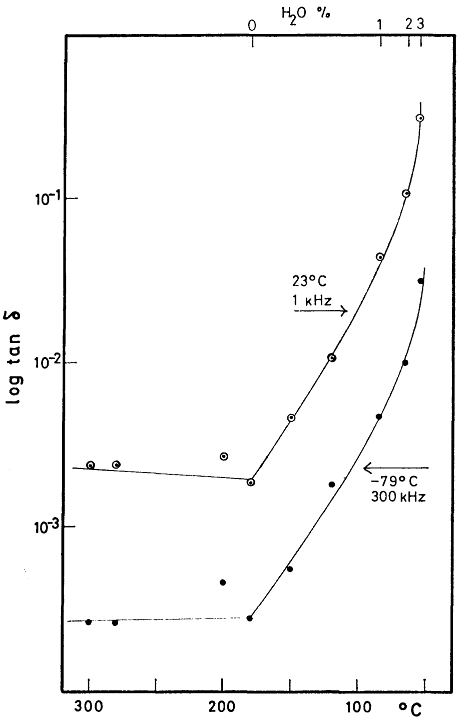

Fig. 11. The relations between tan δ and heat-treatment temperature of γ-alumina at 1 kHz and 300 kHz at 23 °C and −79 °C respectively.

might be possible to see the effect of water content on tan δ more clearly by replacing the horizontal and vertical coordinate axes of Fig. 8 with those of the heat-treatment temperature below and above 180 °C and of tan δ in the range of these dielectric relaxations respectively, as is seen in Fig. 11. The tan δ curves of 1 kHz at 23 °C and 300 kHz at −79 °C in this figure, being situated in the ranges of Relaxations I and II respectively, become constant above 180 °C. This suggests that Relaxations I and II both disappear at about 180 °C; the choice of this temperature as that of the desorption of adsorbed water, as has been mentioned in the previous section, therefore, seems reasonable. Ebert[2] and Dransfeld[3] vaguely attributed this relaxation to the dipole orientation and the proton migration of adsorbed water respectively. Although it may not be simply concluded that Relaxations I and II originate in the adsorbed water on the basis of the present result alone, it might be possible to draw inferences as follows: 1) The dielectric absorption intensity of Relaxation I is larger than that of Relaxation II; hence, Relaxation I might correspond to the larger weight-decrease, as is seen markedly below about 90 °C in Fig. 1. The effect of the adsorbed water for E and the τ_0 of Relaxation I is similar, to some extent, to that of the dielectric relaxation I of silica gel,[10] which was assigned to adsorbed water. Relaxation I might be related to the adsorbed water, being loosely bound to the surface. 2) Relaxation II is smaller than Relaxation I and might correspond to the smaller weight-decrease below about 190 °C in Fig. 1. The effect of adsorbed water for E and τ_0 of this relaxation is somewhat similar to the dielectric relaxation II of silica gel,[9] which was assigned to surface silanol. Relaxation II might thus be related to some kind of surface hydroxyl group which could be dehydrated very easily from the surface of γ-alumina.

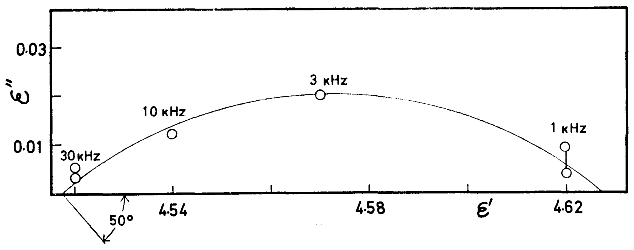

Fig. 12. The Cole-Cole arc of the Relaxation III of γ-alumina at −196 °C.

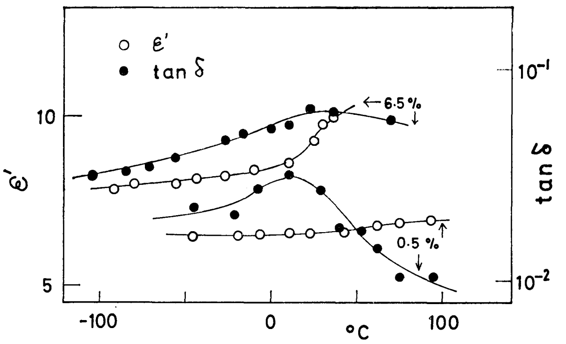

Fig. 13. The relations between tan δ and temperature of γ-alumina with 0.5 and 6.5% water at 9.72 GHz.

Anomaly III. The ε' and ε'' relations of Anomaly III, mentioned in Fig. 3, are plotted at −196 °C in Fig. 12. This relation constitutes the Cole-Cole arc and, therefore, means that Anomaly III is a dielectric relaxation (Relaxation III). The relation between the relaxation times of Relaxation III and the reciprocal temperature plotted in Fig. 6 is linear. Relaxation III becomes observable above the heat-treatment temperature of 120 °C or with a water content of less than 0.5% due to the decrease in the dielectric loss. Relaxation III might thus be related to some kind of hydroxyl group which has a weak interaction with the surroundings, considering the small value of E.

The Dielectric Anomaly at 9.72 GHz. A dielectric anomaly was observed at 9.72 GHz on γ-alumina with various amounts of adsorbed water, as is shown in Fig. 13. This anomaly seems to be a kind of dielectric relaxation according to the temperature effects of ε' and ε'', although the frequency effect could not be measured. We could not ascertain, from the Arrhenius plot in Fig. 6, whether this relaxation belongs to Relaxation II or to III. This relaxation seems, however, to belong to Relaxation II, in view of the similarity of the values of ε' and tan δ.